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(54) Title: WIDE ELECTROCHEMICAL WINDOW SOLVENTS FOR USE IN ELECTROCHEMICAL DEVICES AND ELEC- TROLYTE SOLUTIONS INCORPORATING SUCH SOLVENTS		
(57) Abstract The present invention relates to electrolyte solvents for use in liquid or rubbery electrolyte solutions. Specifically, this invention is directed to boron-containing electrolyte solvents and boron-containing electrolyte solutions.		

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DescriptionWide Electrochemical Window Solvents For Use
In Electrochemical Devices And Electrolyte
Solutions Incorporating Such Solvents

The present application claims priority rights based on U.S. Provisional Application Serial No. 60/006,207 filed November 3, 1995 and U.S. Provisional Application Serial No. 60/006,435 filed November 13, 1995. The present application claims priority rights based on U.S. Nonprovisional Application Serial No. _____, filed on October 31, 1996, which has the same title and inventors as the present application, has attorney identification number P30795, and was transmitted to the U.S. Patent and Trademark Office under Express Mail No. EH682355287US. The present application also claims priority rights based on U.S. Provisional Application Serial No. _____ filed October 24, 1996 which is titled "A Novel Electrolyte Solvent for Rechargeable Lithium and Lithium-Ion Batteries", has the same inventors as the present application, has attorney identification number P30794, and was transmitted to the U.S. Patent and Trademark Office under Express Mail No. EH790578071US. The above-identified applications are hereby incorporated by reference.

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Introduction

This invention relates generally to electrolyte solvents for use in liquid or rubbery polymer electrolyte solutions as are used, for example, in

electrochemical devices. More specifically, this invention is directed to boron-containing electrolyte solvents and boron-containing electrolyte solutions.

Background of the Invention

5 Typical electrolyte solvents for use in liquid or polymer electrolyte solutions include alkyl ethers such as dimethyl ether, diethyl ether, dioxalane, diglyme and tetraglyme; and alkene carbonates such as ethylene carbonate (hereinafter "EC") and propylene carbonate
10 (hereinafter "PC"). These solvents are used to dissolve electrolyte solutes and/or rubberizing polymer additives to form electrolyte solutions which may be used in electrochemical devices.

 Both alkyl ethers and alkene carbonates present
15 significant disadvantages as electrochemical solvents. Specifically, alkyl ethers are relatively volatile, and therefore may evaporate over time. This is a disadvantage in any electrochemical device that is meant to operate for an extended period of time because
20 evaporation of the solvent may change the electrical behavior of the device. Furthermore, such solvents present fire hazards.

 Moreover, alkyl ethers typically have low dielectric constants which discourage solvation of
25 electrolyte salts. Therefore, alkyl ethers generally depend on cation chelation effects to dissolve significant amounts of electrolyte salts. Such compositions, containing limited amounts of electrolyte, tend to have a limited number of available charge carrier ions.
30 Furthermore, when cation solvation is the driving force for forming a solution, the cation transport number will be low. Both paucity of charge carriers and low cation transport values may lead to undesirable polarization effects.

35 Alkene carbonates have higher dielectric constants than alkyl ethers, and therefore are better electrolyte

solvents for liquid or polymer electrolytes. However, PC is not a suitable solvent because it is unstable in the presence of alkali metals, and forms a passivating layer on lithium. EC is also problematic because its melting point is above room temperature, and therefore it must be mixed with compounds that lower its melting temperature to obtain a liquid or rubbery electrolyte. Moreover, both PC and EC form cloudy solutions with alkali metal salts, which are indicative of disadvantageous composition fluctuations or pre-passivation reaction products. Various unsuccessful attempts have also been made to use other organic molecules, such as ketones, as electrolyte solvents. These attempts were unsuccessful because these molecules exhibit poor chemical and electrochemical stability in the presence of alkali metals.

It has never heretofore been appreciated that these Lewis acid boron-containing compounds (hereinafter "boron electrolyte solvents") would function as advantageous electrolyte solvents. Moreover, there was previously no teaching or suggestion that chemically and electrochemically stable boron electrolyte solvent mixtures could be created by adding a boron electrolyte solvent to a conventional electrolyte solvent.

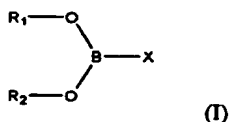
Summary of the Invention

The present invention relates to boron electrolyte solvents, boron electrolyte solvent mixtures and boron electrolyte solutions which all comprise at least one Lewis acid boron-containing compound. The present invention further relates to rechargeable batteries and other electrochemical devices which utilize such electrolyte solutions.

Specifically, the boron electrolyte solvents according to the present invention comprise one or more 3-coordinated boron atoms with Lewis acid characteris-

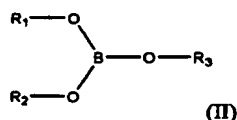
tics. Such boron electrolyte solvents include those with boron linked to oxygen, halogen atoms, sulfur atoms or combinations thereof.

In one specific embodiment of the invention, the boron electrolyte solvent comprises a boron atom bound to two oxygen radicals and one halogen atom as shown below in formula (I):



wherein R_1 and R_2 may be straight or branched chain aliphatic or aromatic alkyl groups and X is a halogen atom. These alkyl groups may have various substituents (e.g. halides) which effectively vary the electronic charge density at the boron atom. It is further preferred for R_1 and R_2 to together form a heterocyclic ring containing an O-B-O linkage.

Preferable boron electrolyte solvents are borate compounds which have at least one BO_2 group such as is shown below in formula (II):



wherein R_1 , R_2 and R_3 may be straight or branched chain aliphatic or aromatic alkyl groups. These alkyl groups may have various substituents (e.g. halides), which effectively vary the electronic charge density at the boron atom. It is further preferred for R_1 and R_2 to together form a heterocyclic ring containing an O-B-O linkage. In one such preferred molecule (hereinafter "BEG-3") according to formula (II), R_1 and R_2 together form a propyl group and R_3 is an isopropyl group.

In a more preferable embodiment of the present invention, the boron electrolyte solvents may comprise borate ethers dimers according to formula (III) below:



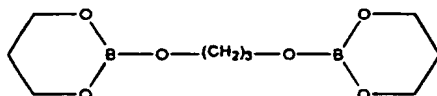
wherein R₁, R₂, R₃ and R₄ may be straight or branched chain aliphatic or aromatic alkyl groups. These alkyl groups may have various substituents (e.g. halides) which effectively vary the electronic charge density at the boron atoms. It is further preferred for R₁ and R₂, and R₃ and R₄, respectively, to together form two heterocyclic rings containing O-B-O linkages. In one such preferred molecule (hereinafter "BEG-2") according to formula (III), R₁ and R₂, and R₃ and R₄, respectively, together form two propyl groups.

A most preferred class of borate ether-type boron electrolyte solvents has a B-O-Z-O-B linkage as shown below in formula (IV):



wherein R₁, R₂, R₃ and R₄ may be straight or branched chain aliphatic or aromatic alkyl groups. These groups may be substituted with various substituents of differing electronegativity, (e.g. halides) which effectively vary the electronic charge density on the boron atoms. It is further preferred for R₁ and R₂, and R₃ and R₄, respectively to together form two heterocyclic rings containing O-B-O linkages. "Z" may be a straight or branched chain aliphatic or aromatic alkyl group which may also be substituted with various groups of different electronegativity. "Z" may also be a siloxane group such as dimethyl siloxane or another bivalent radical. In one such preferred molecule

(hereinafter "BEG-1") according to formula (IV), R_1 and R_2 , and R_3 and R_4 , respectively, together form two propyl groups, and Z is $(CH_2)_3$. The chemical structure of BEG-1 is shown below:



BEG-1

5 Boron electrolyte solvent mixtures according to the invention comprise a boron electrolyte solvent which functions as an electrolyte solvent together with a conventional electrolyte solvent (e.g., an alkene carbonate or an alkyl ether). Boron electrolyte
10 solutions comprise an electrolyte solute (such as an electrolyte salt) dissolved in a boron electrolyte solvent or in a boron electrolyte solvent mixture. Boron electrolyte solutions according to the invention preferably comprise less than 50 mole percent, and more
15 preferably less than 30 mole percent electrolyte solute.

The boron electrolyte solvents and boron electrolyte solvent mixtures of the present invention:

- 20 (i) exhibit unexpectedly superior electrochemical stability against anodic decomposition compared to conventional electrochemical solvents;
- (ii) exhibit unexpectedly superior chemical stability against degradation in the
25 presence of alkali metals;
- (iii) are capable of dissolving large mole fractions of most electrolyte solutes, including alkali metal salts, to provide
30 high room temperature conductivity boron electrolyte solutions;

- 5 (iv) are glass-forming liquids (i.e. liquids which are resistant to crystallization with or without an electrolyte solute salt) at room temperature and down to the glass transition temperature of about -70°C, thus enabling use at low temperatures;
- 10 (v) exhibit higher boiling points and correspondingly lower ambient temperature volatilities than most conventional electrolyte solvents, thus reducing the possibility of volatilization of the electrolyte solvent; and
- 15 (vi) exhibit wide electrochemical windows, enabling use over a wide voltage range.

A particularly effective boron electrolyte solvent mixture may be obtained by mixing together one or more of the above-described boron electrolyte solvents with an alkene carbonate. Such a boron electrolyte solvent mixture has a lower viscosity and remarkably improved electrochemical stability compared to a conventional electrolyte solvent which solely contains an alkene carbonate. Examples of such boron electrolyte solvent mixtures with alkene carbonates include, but are not limited to, a mixture of 1 part by weight BEG-1 mixed with 2 parts by weight EC (hereinafter "1:2 Mix BEG-1:EC"); 1 part by weight BEG-2 mixed with 2 parts by weight EC (hereinafter "1:2 Mix BEG-2:EC"); and corresponding PC mixtures.

In a further advantageous embodiment of the invention, the boron electrolyte solvent mixture or electrolyte solution of the invention may further comprise a polymer which imparts a rubbery consistency. Such rubbery electrolytes are known as "gel electrolytes." Moreover, it is possible to form

polymeric boron compounds which simultaneously function as rubberizing constituents and as electrolyte solvents.

These and other features, aspects and advantages of the present invention will become better understood with reference to the following description, and accompanying drawings.

Brief Description of the Drawings

Figure 1 is a plot of log conductivity (Scm^{-1}) versus reciprocal temperature (K) for various mole percentages of LiClO_4 dissolved in BEG-1.

Figure 2 is a plot of log conductivity (Scm^{-1}) versus mole fraction of dissolved LiClO_4 in BEG-1 at various temperatures ($^{\circ}\text{C}$).

Figure 3 is a plot of log conductivity (Scm^{-1}) versus reciprocal temperature (K) for various molarities of $\text{LiN}(\text{SO}_2\text{CF}_3)_2$ dissolved in BEG-1.

Figure 4 is an overlay of two cyclic voltammograms for the BEG-1 solvent, and for a 2.5M LiClO_4 solution in the 1:2 Mix BEG-1:EC solvent.

Figure 5 is an overlay of three cyclic voltammograms for a 2.5M LiClO_4 solution in the 1:2 Mix BEG-1:EC solvent compared with a conventional 1.0M LiClO_4 solution in a 1:1 mixture of dimethyl ether:EC and a conventional 3.1M LiClO_4 solution in EC.

Figure 6 is an overlay plot of two cyclic voltammograms for a 1.0M LiClO_4 solution in 1:2 Mix BEG-1:PC compared with a conventional 1.0M LiClO_4 solution in PC.

Figure 7 is an overlay plot of log conductivity (Scm^{-1}) versus reciprocal temperature (K) for a 2.5M LiClO_4 solution in 1:2 Mix BEG-1:EC solvent, and the same composition further containing 20 percent by weight polyvinyl acetate (PVAc).

Figure 8 is an overlay plot of log conductivity (Scm^{-1}) versus reciprocal temperature (K) for solutions of 1.0M and 2.5M LiClO_4 , $\text{LiN}(\text{SO}_2\text{CF}_3)_2$, and LiSO_2CF_3 in 1:2 Mix BEG-1:EC.

5 Figure 9 is an overlay plot of log conductivity (Scm^{-1}) versus reciprocal temperature (K) for 2.5M solutions of LiClO_4 in 1:2 Mix BEG-1:EC, 1:2 Mix BEG-2:EC and 1:2 Mix BEG-3:EC.

10 Figure 10 is an overlay plot of three cyclic voltammograms for 1.0M LiClO_4 solutions in 1:2 Mix BEG-1:EC, 1:2 Mix BEG-2:EC and 1:2 Mix BEG-3:EC.

15 Figure 11 is a plot of cell voltage versus time for the first discharge/charging cycle for a Li/2.5M $\text{LiN}(\text{SO}_2\text{CF}_3)_2$ in 1:2 Mix BEG-1:EC gel electrolyte (containing 20 weight percent PVAc)/Li x Mn_2O_3 battery.

20 Figure 12 is a plot of cell voltage versus time for several discharge/charging cycles for a Li/2.5M $\text{LiN}(\text{SO}_2\text{CF}_3)_2$ in 1:2 Mix BEG-1:EC gel electrolyte (containing 20 weight percent PVAc)/Li x Mn_2O_3 battery.

20 Figure 13 is a plot of cell voltage versus time for several discharge/charging cycles for a C/11.0M LiClO_4 in 1:2 Mix BEG-1:EC electrolyte (containing 20 weight percent polymethylmethacrylate) (Aldrich MW=120,000) LiCoO_2 (Alfa, 98%).

25 Detailed Description of the Invention

As used herein, the term "boron electrolyte solvent" refers to a Lewis acid boron-containing compound, with one or more 3-coordinated boron atoms, which is capable of dissolving an electrolyte solute.

30 As used herein, the term "boron electrolyte solvent mixture" refers to a mixture of two or more electrolyte solvents which comprises at least one boron electrolyte solvent according to the present invention.

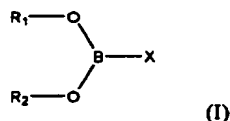
35 As used herein, the term "electrolyte solute" refers to a conductive species, such as a salt, which

behaves as an electrolyte (i.e., transports an electric current via long range motion of ions), and may be dissolved in the boron electrolyte solvent or boron electrolyte solvent mixture.

5 As used herein, the term "boron electrolyte solution" refers to a combination of an electrolyte solute and a boron electrolyte solvent or boron electrolyte solvent mixture.

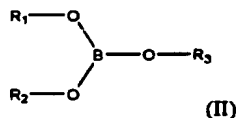
10 As used herein, the term "electrochemical device" is meant to refer to any apparatus that uses an electrolyte.

In one embodiment of the present invention, the boron electrolyte solvent comprises a compound according to formula (I) below:



15 where R_1 and R_2 may be straight or branched chain aliphatic or aromatic alkyl groups and X is a halogen atom. These alkyl groups may have various substituents (e.g. halides) which effectively vary the electronic charge density at the boron atom. It is further
20 preferred for R_1 and R_2 to together form a heterocyclic ring containing an O-B-O linkage.

Preferable boron electrolyte solvents are borate compounds according to formula (II) below:

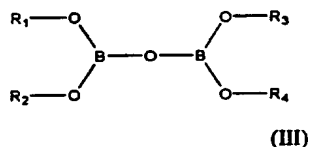


25 wherein R_1 , R_2 and R_3 may be straight or branched chain aliphatic or aromatic alkyl groups. These alkyl groups may have various substituents (e.g. halides), which effectively vary the electronic charge density at the boron atom. It is further preferred for R_1 and R_2 to

together form a heterocyclic ring containing an O-B-O linkage. It may also be possible to synthesize advantageous boron electrolyte solvents analogous to those of formula (II) wherein the oxygen atoms are replaced by sulfur.

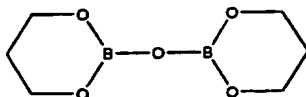
As demonstrated in Example 2, borate compounds according to formula (II) are preferably synthesized by reacting B_2O_3 with an OH group-containing molecule such as an alcohol or a diol. More preferable borate ethers according to formula (II) are synthesized by reacting B_2O_3 with 1,2-propane diol or 1,3-propane diol.

In a more preferable embodiment of the present invention, the boron electrolyte solvents may comprise borate ether dimers according to formula (III) below:



wherein R_1 , R_2 , R_3 and R_4 may be straight or branched chain aliphatic or aromatic alkyl groups. These alkyl groups may have various substituents (e.g. halides) which effectively vary the electronic charge density at the boron atoms. It is still further preferred for R_1 and R_2 , and R_3 and R_4 , respectively, to together form two heterocyclic rings containing O-B-O linkages.

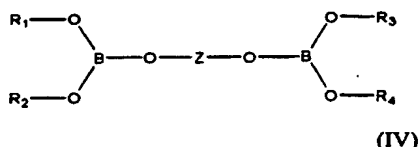
In another preferred embodiment of the invention, a boron electrolyte solvent according to formula (III) is synthesized by reacting B_2O_3 with 1,3-propane diol as described in example 5. The product formed is the boron ether shown below:



BEG-2

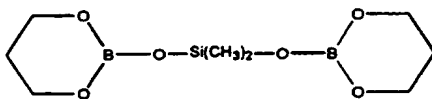
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In a most preferred embodiment of the invention, the boron electrolyte solvents may be borate ether dimers according to formula (IV) below:



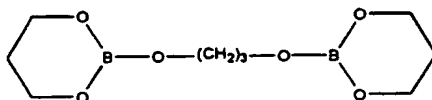
wherein R_1 , R_2 , R_3 , and R_4 may be straight or branched chain aliphatic or aromatic alkyl groups. These groups may be substituted with various substituents of differing electronegativity, (e.g. halides) which effectively vary the electronic charge density on the boron atoms. It is further preferred for R_1 and R_2 , and R_3 and R_4 , respectively, together to form heterocyclic rings containing O-B-O linkages. "Z" may be a straight or branched chain aliphatic or aromatic alkyl group, which may also be substituted with various groups of different electronegativity. "Z" may also be a siloxane group such as dimethyl siloxane or another bivalent radical.

A preferred electrolyte solvent according to formula IV is synthesized by reacting $(\text{CH}_3)_2\text{Si}(\text{OH})_2$ with H_3BO_3 and 1,3-propane diol as shown in Example 4. The product (hereinafter "BEG-4") formed is shown below:



BEG-4

A most preferred boron electrolyte solvent according to formula IV is synthesized by reacting $\text{B}(\text{OH})_3$ with a diol compound as shown in Example 3. Most preferable diols are 1,2-propane diol and 1,3-propane diol. The product formed by reacting $\text{B}(\text{OH})_3$ with 1,3-propane diol (hereinafter "BEG-1") is shown below:



BEG-1

In another embodiment of the present invention, an electrolyte solute is added to a boron electrolyte solvent or solvent mixture to form a boron electrolyte solution. Preferable electrolyte solutes include ionic salts such as LiAlCl_4 , LiClO_4 , $\text{LiN}(\text{SO}_2\text{CF}_3)_2$, LiSO_3CF_3 , and their corresponding sodium analogues. Boron electrolyte solutions containing LiClO_4 are desirable because they produce very high conductivity electrolytes. However, solutions of $\text{LiN}(\text{SO}_2\text{CF}_3)_2$ are more preferable for consumer applications because $\text{LiN}(\text{SO}_2\text{CF}_3)_2$ is chemically more stable than LiClO_4 , and presents no explosion hazard, as does LiClO_4 . Moreover, as shown in Fig. 8, $\text{LiN}(\text{SO}_2\text{CF}_3)_2$ -containing boron electrolyte solutions also exhibit relatively high conductivities. In a preferred boron electrolyte solution, LiClO_4 is dissolved in BEG-1. Figs. 1 and 2 show that room temperature conductivities of a 9.1 mole percent LiClO_4 solution in BEG-1 may approach 10^{-4} Scm^{-1} at room temperature. Figure 8 shows that a 1.0M LiClO_4 solution in 1:2 Mix BEG-1:EC has a conductivity of about $10^{-2.3} \text{ Scm}^{-1}$ at room temperature. In another preferred boron electrolyte solution, LiAlCl_4 was dissolved in a mixture of BEG-1 and EC. Although LiAlCl_4 decomposes in most organic solvents and in pure BEG-1, it does not decompose in mixtures of BEG-1 and EC.

BEG-1 and BEG-2 have symmetrical structures, and therefore may have small dielectric constants. However, BEG-1 and BEG-2 are very good solvents for alkali metal salt electrolyte solutes. For example,

BEG-1 dissolves up to 50 mole percent of LiClO_4 at ambient temperature to yield a viscous solution.

Without limiting the invention to any particular theory of operation, it is theorized that the
5 interaction between the ClO_4^- oxygen atoms and the electron-deficient boron atom drives the dissolution.

Solutions of LiClO_4 in BEG-1 and BEG-2 tend to be substantially transparent, which indicates that LiClO_4 may dissolve better in BEG-1 and BEG-2 than in known
10 ether or carbonate solvents, which often yield cloudy solutions. Cloudy electrolyte solutions are unsuitable for some applications, such as optical displays.

In yet another aspect of the present invention, a conventional solvent such as an alkene carbonate or
15 an alkyl ether may be added to a boron electrolyte solvent to form a boron electrolyte solvent mixture. The preferred electrolyte solvent mixture "1:2 Mix BEG-2:EC" is formed by mixing 1 part by weight BEG-2 with 2 parts EC. The most preferred electrolyte
20 solvent mixture "1:2 Mix BEG-1:EC" is formed by mixing 1 part BEG-1 with 2 parts EC.

As shown in Figure 7, high molecular weight polymers may also be added to electrolyte solutions to form gel electrolytes which exhibit more desirable
25 rubbery behavior. It is preferable to use polymers with sufficiently high molecular weight to impart a rubbery consistency to the electrolyte. Preferred polymers include high molecular weight polyethylene oxide having a molecular weight of at least about 10^6
30 and polyvinyl acetate having a molecular weight of more than 50,000.

Further, polymer oils may be synthesized by reacting boron electrolyte solvents such as BEG-1 with silicates as shown in Example 14. In yet another
35 aspect of the present invention, polymeric Lewis acid

borate compounds may be synthesized as shown in Example 15.

5 Ionic conductivities of the boron electrolyte solutions according to the present invention were determined from complex impedance plots obtained using twin platinum electrode dip-type cells with cell constants of about $1\text{-}2\text{ cm}^{-1}$. The complex impedance plots were generated using a HEWLETT-PACKARD Model HP4192A-Frequency Analyzer. Measurements were
10 automated to cover a predetermined temperature range at a sequence of temperatures controlled by a EURO THERM temperature controller.

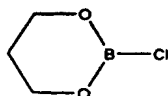
The cyclic voltammograms shown in Figs. 4-6 and 10 were obtained using a PAR Potentiometer. All scans
15 were performed at room temperature with a scan speed of 10mV/s . A platinum pseudo-reference electrode was used for all the scans.

The boron electrolyte solvents and boron electrolyte solutions described herein are useful in
20 all manner of electrochemical devices which require electrolytes. Some examples of electrochemical devices which require electrolytes include batteries, fuel cells, photochromic displays, photovoltaic cells and gas sensors. This list is merely exemplary, and is not
25 meant to limit the invention to any particular electrochemical device.

Specific embodiments of boron electrolyte solvents, boron electrolyte solvent mixtures, and solutions in accordance with the present invention
30 will now be described in detail. These examples are intended to be illustrative, and the invention is not limited to the materials or amounts set forth in these embodiments.

Example 1Preparation of a Boron Electrolyte
Solvent According to Formula (I)

A boron electrolyte solvent according to
5 formula (I) was synthesized. The product formed
(hereinafter "BEG-5") is shown below:



BEG-5

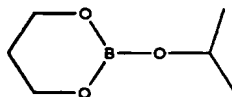
BEG-5 was prepared by the following procedure disclosed
by A. Finch, J.C. Lockhart and E.J. Pearn in J. Org.
Chem., 26, pp. 3250-53 (1961). 15.2 grams (0.20 moles)
10 of 1,3-propanediol (Aldrich, 98%) was added dropwise to
a solution of 23.5 grams (0.20 moles) boron trichloride
(Aldrich, 1M in heptane) diluted in 60 mL methylene
chloride (Baker) at 5°-10°C. Nitrogen was bubbled
through the flask to remove HCl generated by the
15 reaction. The reaction was allowed to proceed for
6 hours. Vacuum-distillation at 30°-31°C/0.15 mmHg
yielded 15.9 grams of the product shown above (yield
66% based on BCl₃).

Example 2

20

Preparation of a Boron Electrolyte
Solvent According to Formula (II)

A boron electrolyte solvent according to
formula (II) was synthesized. The product formed
(hereinafter "BEG-3") is shown below:

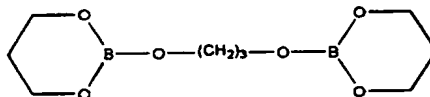


BEG-3

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BEG-3 was prepared by the following procedure. 13.92 grams (0.20 mole) of B_2O_3 (Aldrich, 99.98%) and 30.40 grams (0.40 mole) of 1,3-propanediol (Aldrich, 98%) were mixed in approximately 50 mL toluene and
5 refluxed in a flask equipped with water separation apparatus until no further water was generated. The total amount of water separated at this stage was approximately 7.3 mL. Then 26.40 grams (0.44 mole) of isopropanol (Aldrich, 99%) was added, and an additional
10 3.6 mL of water was collected. The resultant product was then refluxed in the presence of lithium overnight. Vacuum-distillation at $67^\circ\text{--}68^\circ\text{C}/0.4$ mmHg yielded 38.0 grams of the product shown above (yield 66% based on B_2O_3).

15

Example 3Preparation of a Boron Electrolyte Solvent According to Formula (IV)

BEG-1

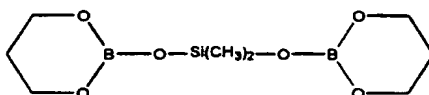
A more preferred boron electrolyte solvent according to formula (IV) was synthesized as follows.
20 18.55 grams (0.30 mole) of H_3BO_3 (Allied Chemical, 99.89%) and 34.25 grams (0.45 mole) of 1,3-propanediol (Aldrich, 98%) were mixed along with approximately 80 mL of toluene in a flask equipped with water-separation apparatus. After refluxing for 8 hrs a total amount of
25 16.8 mL of water was separated. The resultant product was then refluxed in the presence of lithium overnight. Most of the solvent was removed by a rotation evaporator, and the remaining solvent was removed by vacuum-distillation. A fraction collected at
30 $125^\circ\text{--}128^\circ\text{C}/0.05$ mmHg yielded approximately 29.6 grams (81% based on H_3BO_3).

-18-

BEG-1 is a viscous, glass-forming liquid with a T_g of -80°C and a boiling point of $125-128^\circ\text{C}/0.05\text{ mmHg}$, implying 380°C at 760 mmHg . A previous report of the preparation of this substance reports a boiling point of $165-169^\circ\text{C}$ at 10.6 mmHg , implying 390°C at 760 mmHg .
5 See H. Steinberg, Organoboron Chemistry, Vol. 1, Ch 5, (1964).

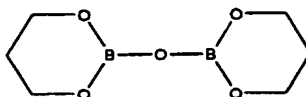
Example 4

10 Preparation of a Second Boron Electrolyte Solvent According to Formula (IV)



BEG-4

A preferred boron electrolyte solvent according to formula (IV) was synthesized as follows. 14.2 grams (0.11 mole, Aldrich, 99%) of $(\text{CH}_3)_2\text{SiCl}_2$ was hydrolyzed by adding it to 30 mL of deionized water, and the
15 product was extracted with 60 mL of ethyl ether. The organic phase was washed with deionized water until the pH reached 7, followed by evaporation of the ethyl ether. 1,3-propanediol (16.8 grams, 0.22 mole, Aldrich, 98%), H_3BO_3 (13.6 grams, 0.22 mole, Allied
20 Chemical, 99.89%) and toluene (80 mL) were added to the resultant $(\text{CH}_3)_2\text{Si}(\text{OH})_2$, and refluxed until no further water was separated out (approximately 8 hrs). The mixture was further refluxed in the presence of metal lithium overnight, and the solvent was removed by
25 using a rotation evaporator. The product was obtained in a yield of 40 percent versus H_3BO_3 , by collecting the fraction of $150-155^\circ\text{C}/1\text{ mmHg}$.

Example 5Preparation of a Boron Electrolyte Solvent According to Formula (III)

BEG-2

A preferred boron electrolyte solvent according to formula (III) was synthesized as follows. 13.92 grams (0.20 mole) of B_2O_3 (Aldrich, 99.98%-) and 30.40 grams (0.40 mole) of 1,3-propanediol (Aldrich, 98%) were reacted in a similar manner to that described in Example 2. The amount of water finally separated was 7.3 mL. During vacuum-distillation the fraction of 138°-143°C/0.05 mmHg was collected with yield of 27.84 grams (75% based on B_2O_3).

Example 6Unexpected Stability of Boron Electrolyte Solvent Mixtures

A boron electrolyte solvent mixture was prepared by mixing 1 part by weight BEG-1 prepared according to Example 3 with two parts ethylene carbonate. A second boron electrolyte solvent mixture was prepared by mixing 1 part by weight BEG-1 with two parts by weight propylene carbonate. A third boron electrolyte solvent mixture was prepared by mixing 1 part by weight BEG-1 with one part by weight of acetone, which is a simple type of ketone. All reagents were mixed and weighed out in a dry box.

Vials containing pieces of shiny lithium foil immersed in the above-described electrolyte solvent mixtures were sealed tightly and put aside for observation. Control samples were prepared by immersing pieces of shiny lithium foil in the ethylene carbonate,

propylene carbonate and acetone-containing solvent mixtures.

The acetone-containing vials were left overnight at ambient temperature. The ethylene carbonate and propylene carbonate-containing vials were heated to 90°C in an oven overnight.

In all the control samples, a white precipitate was observed in the vial. This result indicates, as expected, that the solvent reacted with the alkali metal. However, the boron electrolyte solvent mixtures with ethylene carbonate and propylene carbonate remained completely clear for days, and the lithium foil remained bright and shiny.

This result indicates that the boron electrolyte solvent prevented the ethylene carbonate or the propylene carbonate from reacting with the lithium metal. The boron electrolyte solvent mixture with acetone did show some degradation in the presence of lithium. However, the degradation was greatly inhibited compared to the acetone control sample.

Example 7

Preparation of Boron Electrolyte Solvent Mixtures

One part by weight BEG-1 prepared according to Example 3 was mixed with two parts by weight EC to form a boron electrolyte solvent mixture "1:2 Mix BEG-1:EC."

One part by weight BEG-1 prepared according to Example 3 was mixed with two parts by weight PC to form a boron electrolyte solvent mixture "1:2 Mix BEG-1:PC."

One part by weight BEG-2 prepared according to Example 5 was mixed with two parts by weight EC to form a boron electrolyte solvent mixture "1:2 Mix BEG-2:EC."

One part by weight BEG-3 prepared according to Example 2 was mixed with two parts by weight EC to form a boron electrolyte solvent mixture "1:2 Mix BEG-3:EC."

Example 8Preparation of LiClO₄ BEG-1
Boron Electrolyte Solutions

Various concentrations of LiClO₄ boron electrolyte
5 solutions were prepared by dissolving LiClO₄ in BEG-1,
which was prepared according to Example 3. All mate-
rials were weighed out in a glove box. Fig. 1 shows a
plot of the log of conductivity versus reciprocal
temperature for these electrolytes. Fig. 2 shows a
10 plot of the log of conductivity versus mole fraction
LiClO₄ at 30°C, 50°C, 100°C and 150°C.

The solution with the highest room temperature
conductivity contained 9.1% LiClO₄, and has a
conductivity below 10⁻⁴ Scm⁻¹. Fig. 1 shows that the
15 solution of 75 mole percent LiClO₄ in BEG-1 was only
thermodynamically stable as a liquid above 80°C.

Fig. 4 shows an overlay of two cyclic volta-
mmograms obtained for a 2.5 M LiClO₄ Mix BEG-1:EC boron
electrolyte solution and for pure BEG-1 solvent. The
20 cyclic voltammogram for the boron electrolyte solution
indicates that lithium can be deposited and stripped
back into the solution in an almost reversible fashion.
This property is important for rechargeable electro-
chemical devices using these electrolytes.

25 Fig. 4 also shows that the 2.5 M LiClO₄ 1:2 Mix
BEG-1:EC electrolyte solution solvent exhibited a wide
electrochemical window of about 5.3 volts. This
observed voltage window is believed to be limited by
the stability of the ClO₄⁻ anion and the Li⁺ cation in
30 the solution, rather than by the solvent.

Example 9

Preparation of $\text{LiN}(\text{SO}_2\text{CF}_3)_2$
Boron Electrolyte Solutions in
1:2 Mix BEG-1:EC Electrolyte Solvent

5 $\text{LiN}(\text{SO}_2\text{CF}_3)_2$ was added to a BEG-1 electrolyte solvent mixture in amounts sufficient to form 0.5 to 6.0M boron electrolyte solutions. All of these solutions were clear.

10 Fig. 3 shows a plot of the log of conductivity versus reciprocal temperature for these boron electrolyte solutions. Fig. 3 indicates that the highest ambient temperature conductivities corresponded to the 0.5 or 1.0M boron electrolyte solutions, which show conductivities of $10^{-3.8} \text{ Scm}^{-1}$. Fig. 3 further
15 showed that the conductivity of the 0.5 and 1.0M solutions remained above 10^{-5} Scm^{-1} down to 0°C .

Example 10

Comparison of Boron Electrolyte Solutions
Containing 1:2 Mix BEG-1:EC and Boron Electrolyte
20 Solutions Containing Prior Art Electrolytes

 A 2.5M LiClO_4 solution in 1:2 Mix BEG-1:EC was prepared by dissolving an appropriate amount of LiClO_4 in a 1:2 Mix BEG-1:EC boron electrolyte solvent mixture prepared in accordance with Example 7. A 1.0M LiClO_4
25 solution was prepared by dissolving LiClO_4 in a 1:1 mixture of dimethyl ether and EC. A 3.1M LiClO_4 solution was prepared by dissolving an appropriate amount of LiClO_4 in EC. All materials were weighed out in a glove box. Fig. 5 shows an overlay of three
30 cyclic voltammograms for these three electrolyte solutions. Fig. 5 shows that the electrochemical window was much wider for the 1:2 Mix BEG-1:EC solvent than for the dimethyl ether/EC solvent or the EC solvent.

A 1.0M LiClO_4 boron electrolyte solution in 1:2 Mix BEG-1:PC was prepared by dissolving an appropriate amount of LiClO_4 in a 1:2 Mix BEG-1:PC boron electrolyte solvent mixture prepared in accordance with Example 7.

- 5 A 1.0M LiClO_4 :PC solution was prepared by dissolving an appropriate amount of LiClO_4 in PC. Fig. 6 shows an overlay of two cyclic voltammograms for these two electrolyte solutions. Fig. 6 shows that the PC solution began to decompose at about 4.5 volts positive with respect to Li^+/Li . However the boron electrolyte solution did not begin to decompose until about 5.6 volts positive with respect to Li^+/Li .
- 10

Example 11

- 15 Comparison of the Conductivities of Different Alkali Salt Solutions in 1:2 Mix BEG-1:EC

- Boron electrolyte solutions of 1.0M and 2.5M LiClO_4 , $\text{LiN}(\text{SO}_2\text{CF}_3)_2$ and LiSO_3CF_3 were prepared by dissolving appropriate quantities of these salts in 1:2 Mix BEG-1:EC solvent prepared according to Example 7.
- 20 These solutions were then tested to determine their conductivity. Fig. 8 shows that the 1.0 M LiClO_4 solution had the highest conductivity at room temperature. Fig. 8 also shows that the 1.0M solutions had higher conductivity than the 2.5M solutions. Boron electrolyte solutions containing sodium trifluoromethane sulfonate ($\text{CF}_3\text{SO}_3\text{Na}$, Aldrich) had conductivities very similar to those of $\text{LiN}(\text{SO}_2\text{CF}_3)_2$ prepared at the same concentration.
- 25

Example 12

- 30 Comparison of Boron Electrolyte Solutions

Boron electrolyte solutions of 2.5M LiClO_4 were prepared for 1:2 Mix BEG-1:EC solvent, 1:2 Mix BEG-2:EC solvent, 1:2 Mix BEG-3:EC solvent, 1:2 Mix

BEG-4:EC solvent and 1:2 Mix BEG-5:EC solvent. The 2.5M solutions of both the 1:2 Mix BEG-1:EC and 1:2 Mix BEG-2:EC solutions showed high room temperature conductivity. However, the 1:2 Mix BEG-1:EC solvent may be more advantageous for actual devices because it has a wider electrochemical window. The 1:2 Mix BEG-4:EC solution exhibited higher conductivity than the 1:2 Mix BEG-1:EC solution. The 1:2 Mix BEG-5:EC solution exhibited a comparable conductivity to the 1:2 Mix BEG-1 solution.

Fig. 5 shows that an electrochemical decomposition process attributed to EC began at +1 volts with respect to a platinum pseudo-reference electrode. Fig. 10 shows that the onset of the electrochemical decomposition process attributed to EC was not affected by BEG-3-containing boron electrolyte solutions, but was not observed until more positive voltages than +1 volts were applied to BEG-2-containing, BEG-4-containing and BEG-1-containing boron electrolyte solutions. Most remarkably, decomposition attributed to EC was completely suppressed in BEG-1-containing boron electrolyte solutions.

Example 13

Preparation of 1.3 M LiClO₄ Electrolyte Solutions in 1:2 Mix BEG-1:EC Which Incorporate High Molecular Weight Polymers

Electrolytes must exhibit rubbery behavior to be useful in solid state electrochemical devices. Rubbery behavior may be imparted to a boron electrolyte solution by adding a high molecular weight polymer.

A 1.3M LiClO₄ boron electrolyte solution was prepared by dissolving LiClO₄ in a 1:2 Mix BEG-1:EC solvent mixture prepared according to Example 7. A gel electrolyte was similarly prepared by further adding 20% polyvinyl acetate (molecular weight of about

50,000) respectively. Fig. 7 is an overlay plot of log conductivity versus reciprocal temperature which compares the conductivity of the gel electrolyte to the reference boron electrolyte solution which does not contain the polymer. Fig. 7 shows that the addition of 20 weight percent polyvinyl acetate somewhat reduced the room temperature conductivity of the solution. However, it is likely that higher conductivities could have been achieved by adding a smaller percentage of higher molecular weight polymer.

Another electrolyte solution was prepared by adding 5 percent polyethylene oxide (MW about 10^6) to the above-described 1.3 M LiClO_4 boron electrolyte solution. The resultant composition was a high stretch rubbery material which may be useful as an electrolyte for solid state electrochemical devices.

Example 14

Preparation of a Boron Electrolyte Solvent Further Comprising a Silicate

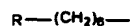
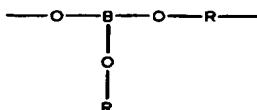
A polymer oil was generated by reacting BEG-1 prepared according to example 3 with tetramethyl orthosilicate. Specifically, 4.88 grams (0.02 mole) of BEG-1 and 0.608 grams (0.004 mole, Aldrich, 99+%) of tetramethyl orthosilicate were sealed in a strong vial, and heated at 250°C overnight. As a result, a polymer oil with a somewhat complicated structure was obtained. This oil may be used as a solvent for non-aqueous electrolytes.

Example 15

Synthesis of a Polymer Borate Compound

A polymeric borate compound according to the following formula was synthesized

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A mixture of H_3BO_3 (12.4 grams, 0.20 moles, Allied Chemical), 1,6 hexane diol (35.5 grams, 0.30 moles, Aldrich, 97%) and toluene (100 mL, Fisher, 99.9%) was refluxed until a quantitative amount of water was separated. The mixture was further refluxed over metal lithium for at least 5 hours, and then the solid residual was filtered out. The solvent was evaporated on a vacuum line to obtain 34.8 grams of viscous liquid (yield: 94%), which became more viscous after cooling down to room temperature.

Example 16

A Rechargeable Li Battery Incorporating a Boron Electrolyte Solution

A voltaic cell was formed using a Li foil anode and a cathode made from LiMn_2O_4 , carbon black, and a binder, separated by a gel electrolyte containing 2.5M $\text{LiN}(\text{SO}_2\text{CF}_3)_2$ dissolved in 1:2 Mix BEG-1:EC electrolyte and 20 weight percent polyvinyl acetate (MW=50,000). This cell was then discharged and charged over several cycles as shown in Figs. 11 and 12. The cell showed reversible behavior over 1000 discharge/charge cycles.

Example 17

A Rechargeable Li Battery Incorporating a Boron Electrolyte Solution

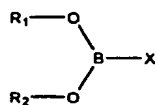
A voltaic cell was formed using a carbon anode and a LiCoO_2 cathode, separated by a gel electrolyte containing 1.0M LiClO_4 dissolved in 1:2 Mix BEG-LiEC electrolyte and 20 weight percent poly (methyl methacrylate). A composite cathode was prepared by

- mixing LiCoO_2 (Alpha, 98%), carbon black, and the above described gel electrolyte in weight ratios of 72:8:20, respectively. The resulting slurry was pressed onto Ni foil. The carbon anode was constructed from
- 5 80 weight percent carbon and 20 weight percent boron electrolyte gel used as a binder. The assembled battery was charged, and then cycled between, 2.5 and 4.4 volts. As shown in Fig. 13, after 14 cycles, the cycling voltage limit was increased to 4.5 volts.
- 10 The cell continued to cycle reversibly, and showed a significant increase in capacity.

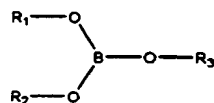
Various publications have been cited herein which are hereby incorporated by reference in their entireties.

Claims

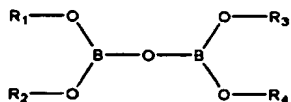
- 1 1. A boron electrolyte solution which comprises:
 2 a. an electrolyte solute, and
 3 b. a boron electrolyte solvent.
- 1 2. A boron electrolyte solution according to claim 1
 2 which comprises less than 50 mole percent of the
 3 electrolyte solute.
- 1 3. A boron electrolyte solution according to claim 2
 2 wherein the boron electrolyte solvent is selected
 3 from the group consisting of compounds of formulas
 4 (I), (II), (III) and (IV):



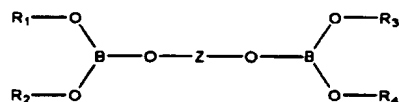
(I)



(II)



(III)



(IV)

- 5 wherein X is a halogen atom, R₁, R₂, R₃ and R₄ are straight
 6 or branched chain aliphatic or aromatic alkyl groups
 7 which may be substituted with substituents of varying
 8 electronegativity, and Z is a straight or branched chain
 9 aliphatic or aromatic alkyl group or siloxane group.

- 1 4. A boron electrolyte solution according to claim 3
2 wherein the electrolyte solute is selected from the
3 group consisting of LiAlCl_4 , LiClO_4 , $\text{LiN}(\text{SO}_2\text{CF}_3)_2$,
4 LiSO_3CF_3 and their corresponding sodium analogues.

- 1 5. A boron electrolyte solution according to claim 3
2 which further comprises a high molecular weight
3 polymer which forms a gel while avoiding significant
4 decrease in conductivity of the boron electrolyte
5 solution.

- 1 6. A boron electrolyte solution according to claim 3
2 which further comprises a boron-free electrolyte
3 solvent.

- 1 7. A boron electrolyte solution according to claim 3
2 wherein the boron electrolyte solvent is selected
3 from the group consisting of compounds of formulas
4 (III) and (IV) wherein R_1 and R_2 , and R_3 and R_4 ,
5 respectively together form two heterocyclic rings
6 containing O-B-O linkages.

- 1 8. A boron electrolyte solution according to claim 7
2 wherein the boron electrolyte solvent is selected
3 from the group consisting of BEG-1, BEG-2, and
4 BEG-4.

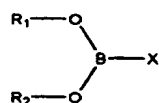
- 1 9. A boron electrolyte solution according to claim 2
2 wherein the boron electrolyte solvent is a polymer
3 borate compound.

- 1 10. An electrochemical device comprising a boron
2 electrolyte solution which comprises:
3 a. an electrolyte solute, and
4 b. a boron electrolyte solvent.

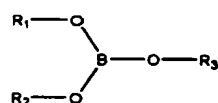
1 11. An electrochemical device according to claim 10
 2 wherein the electrolyte solution comprises less than
 3 50 mole percent of the electrolyte solute.

1 12. An electrochemical device according to claim 11
 2 which further comprises an electrode which comprises
 3 lithium.

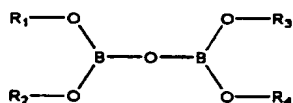
1 13. An electrochemical device according to claim 12
 2 wherein the boron electrolyte solvent is selected
 3 from the group consisting of compounds of formulas
 4 (I), (II), (III) and (IV):



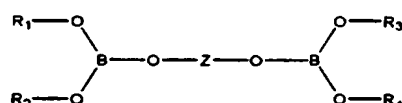
(I)



(II)



(III)



(IV)

5 wherein X is a halogen atom, R₁, R₂, R₃ and R₄ are straight
 6 or branched chain aliphatic or aromatic alkyl groups
 7 which may be substituted with substituents of varying
 8 electronegativity, and Z is a straight or branched chain
 9 aliphatic or aromatic alkyl group or siloxane group.

1 14. An electrochemical device according to claim 13
 2 wherein the electrolyte solute is selected from the
 3 group consisting of LiAlCl₄, LiClO₄, LiN(SO₂CF₃)₂,
 4 LiSO₃CF₃, and their corresponding sodium analogues.

1 15. An electrochemical device according to claim 13
 2 wherein the boron electrolyte solution further
 3 comprises a high molecular weight polymer which

- 4 forms a gel while avoiding significant decrease in
5 conductivity of the boron electrolyte solution.
- 1 16. An electrochemical device according to claim 13
2 wherein the boron electrolyte solution further
3 comprises a boron-free electrolyte solvent.
- 1 17. An electrochemical device according to claim 16
2 wherein the boron electrolyte solvent is selected
3 from the group consisting of compounds of formulas
4 (III) and (IV) wherein R_1 and R_2 , and R_3 and R_4 ,
5 respectively together form two heterocyclic rings
6 containing O-B-O linkages.
- 1 18. An electrochemical device according to claim 17
2 wherein the boron electrolyte solvent is selected
3 from the group consisting of BEG-1, BEG-2, and
4 BEG-4.
- 1 19. An electrochemical device according to claim 10
2 wherein the boron electrolyte solvent is a polymer
3 borate compound.
- 1 20. A method of improving the stability of a lithium-
2 containing electrode which comprises contacting said
3 electrode with a boron electrolyte solvent.

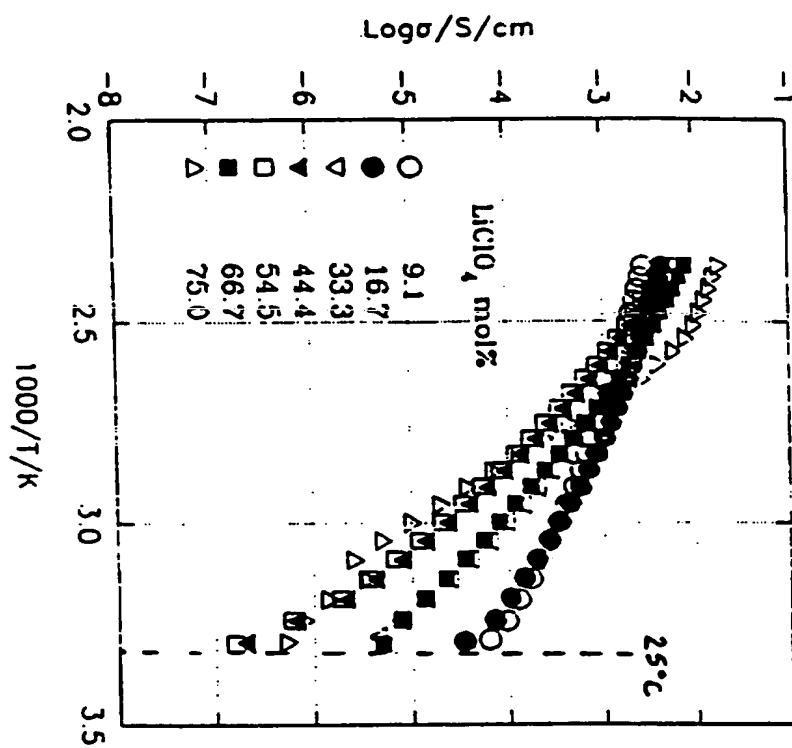
1/13
FIGURE 1

FIGURE 2

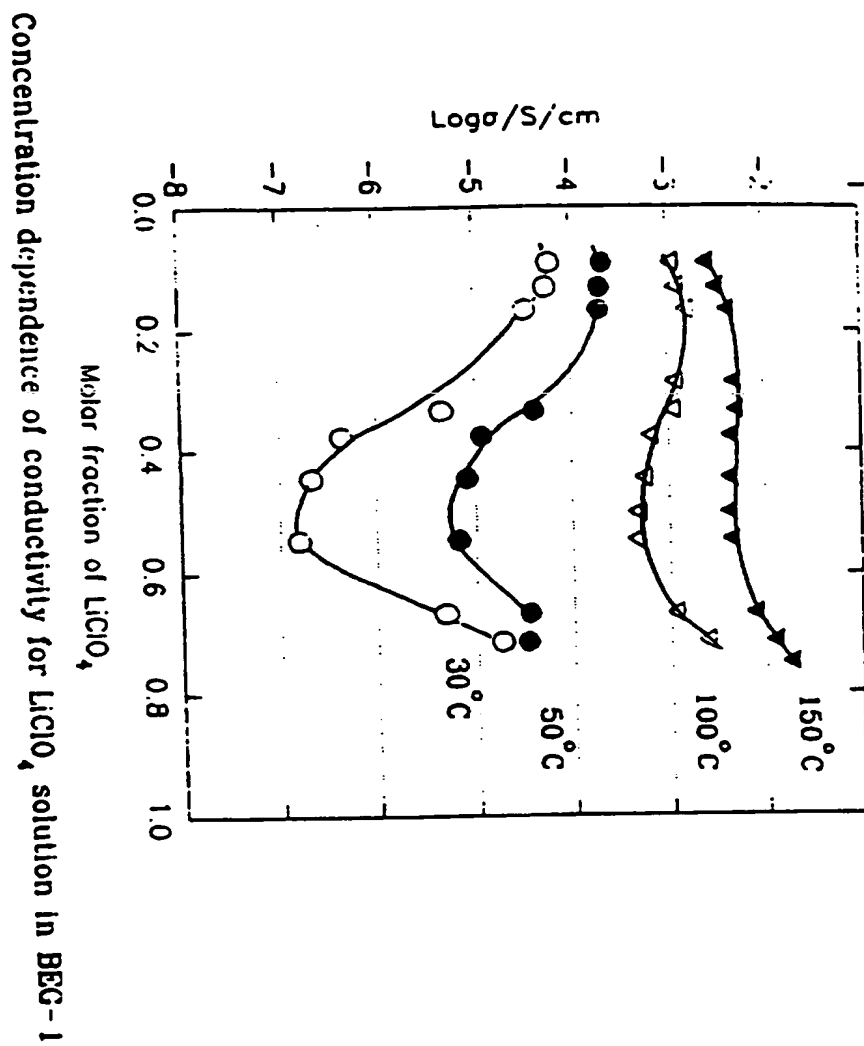
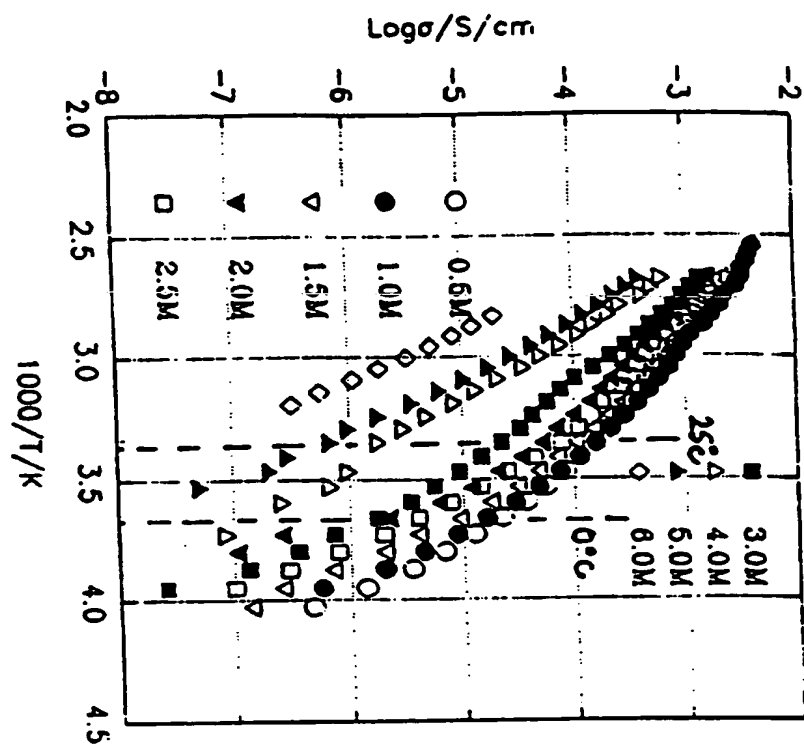


FIGURE 3



Conductivity of $\text{LiN}(\text{SO}_2\text{CF}_3)_2$ solution in BEG-1

FIGURE 4

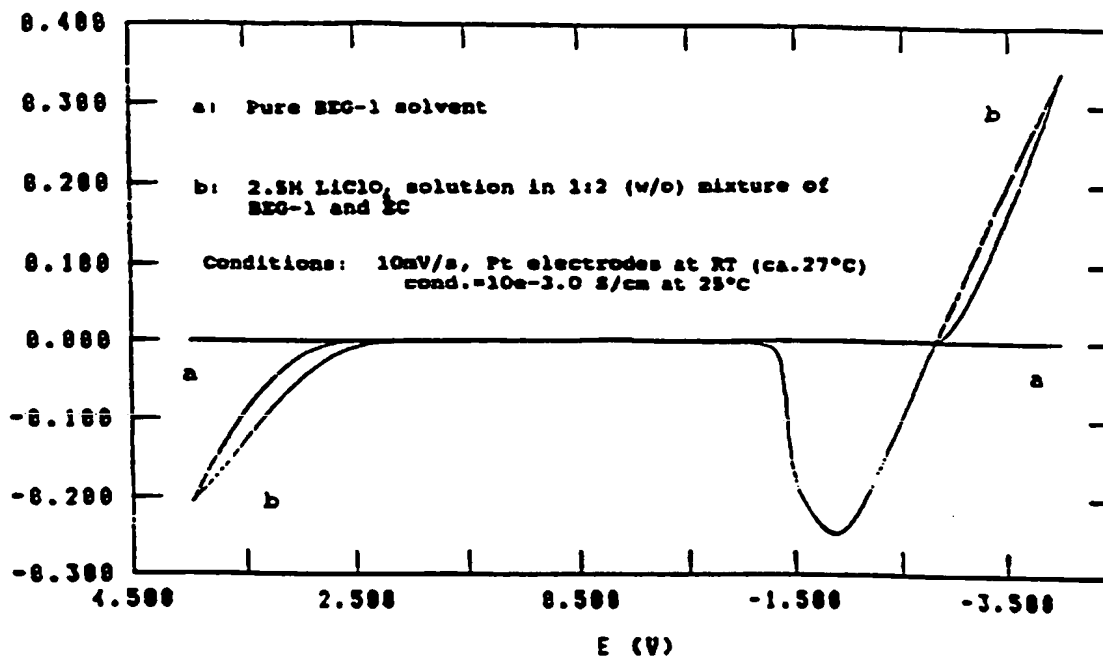
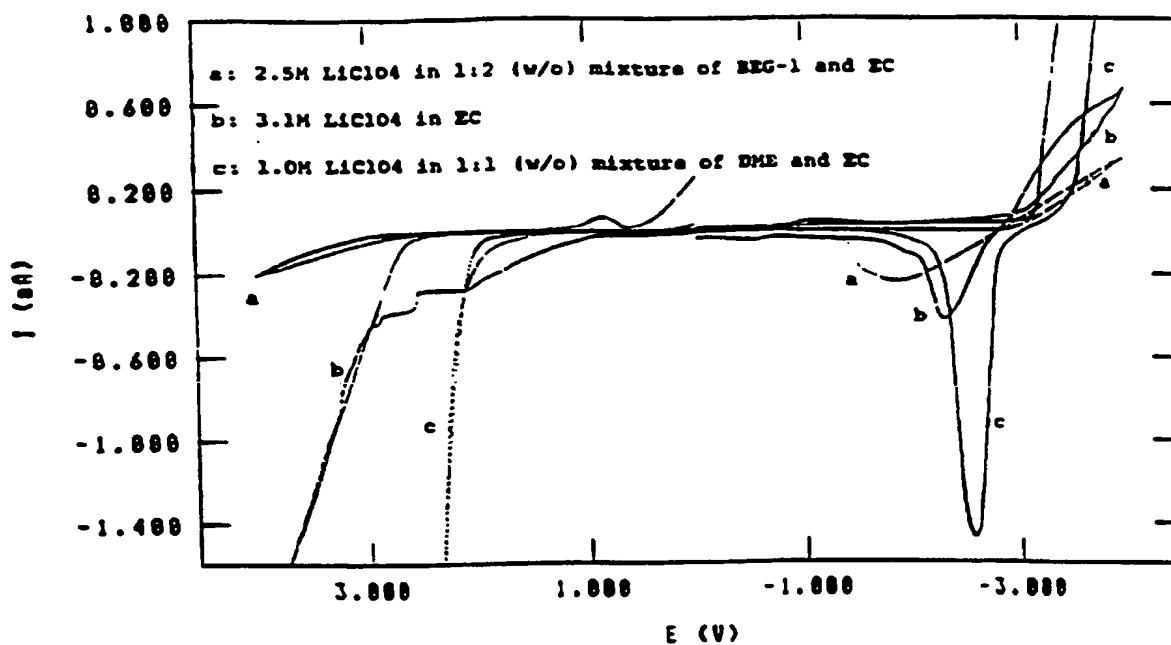


FIGURE 5



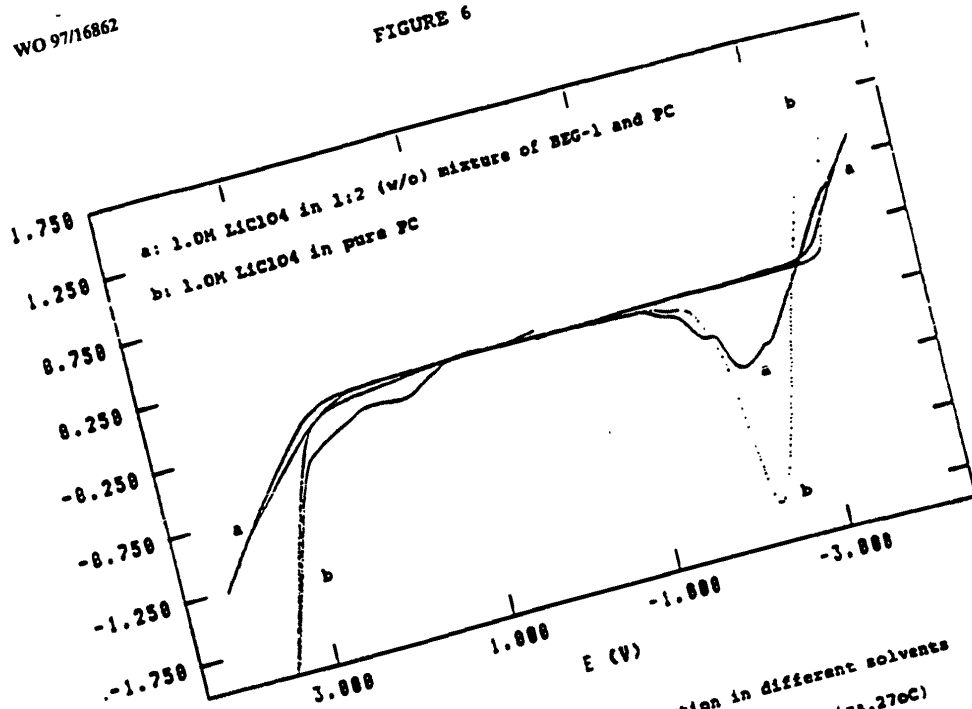
Cyclic voltammogram of LiClO4 solution in different solvents

Scan rate = 10mV/s, Pt electrodes, at room temperature (ca. 27°C)

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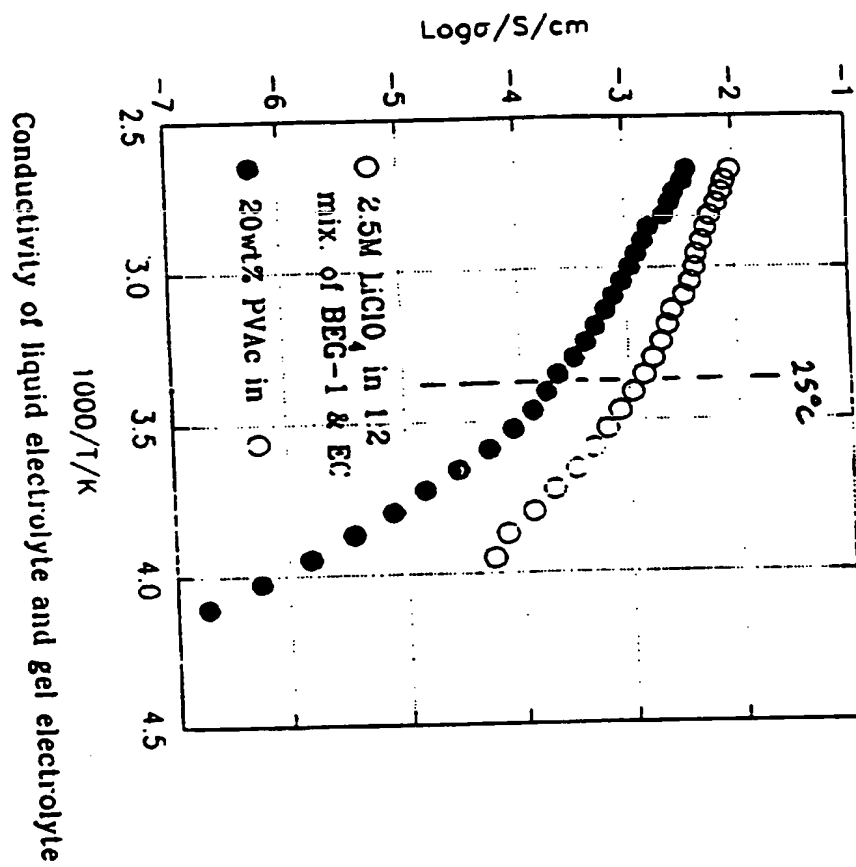
FIGURE 6



Cyclic voltammogram of LiClO₄ solution in different solvents
Scan rate = 10mV/s, Pt electrodes, at room temperature (ca.27°C)

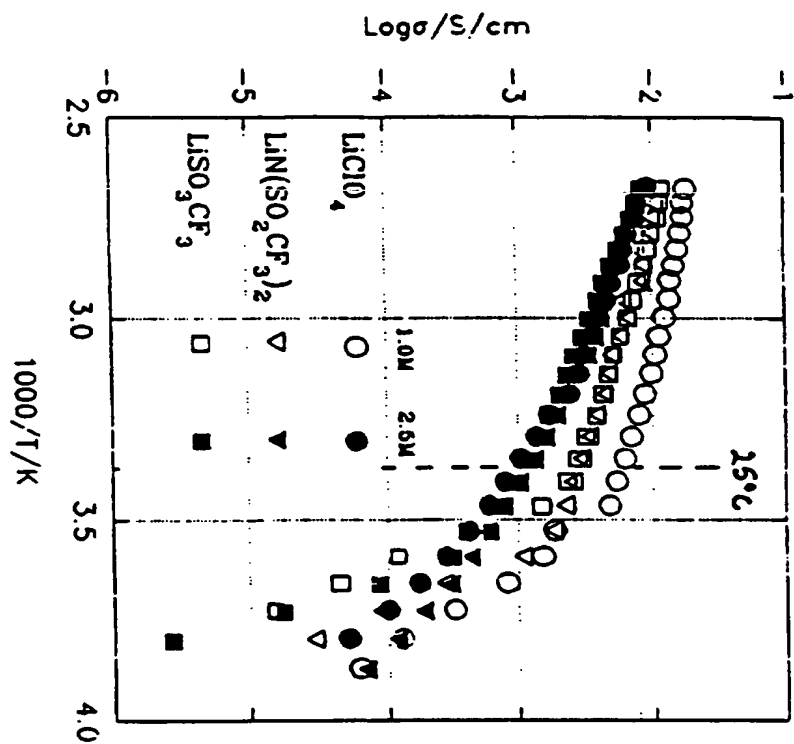
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FIGURE 7



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FIGURE 8



Conductivity of different salt solutions in 1:2 (w/o) mixture of BEG-1 and EC

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FIGURE 9

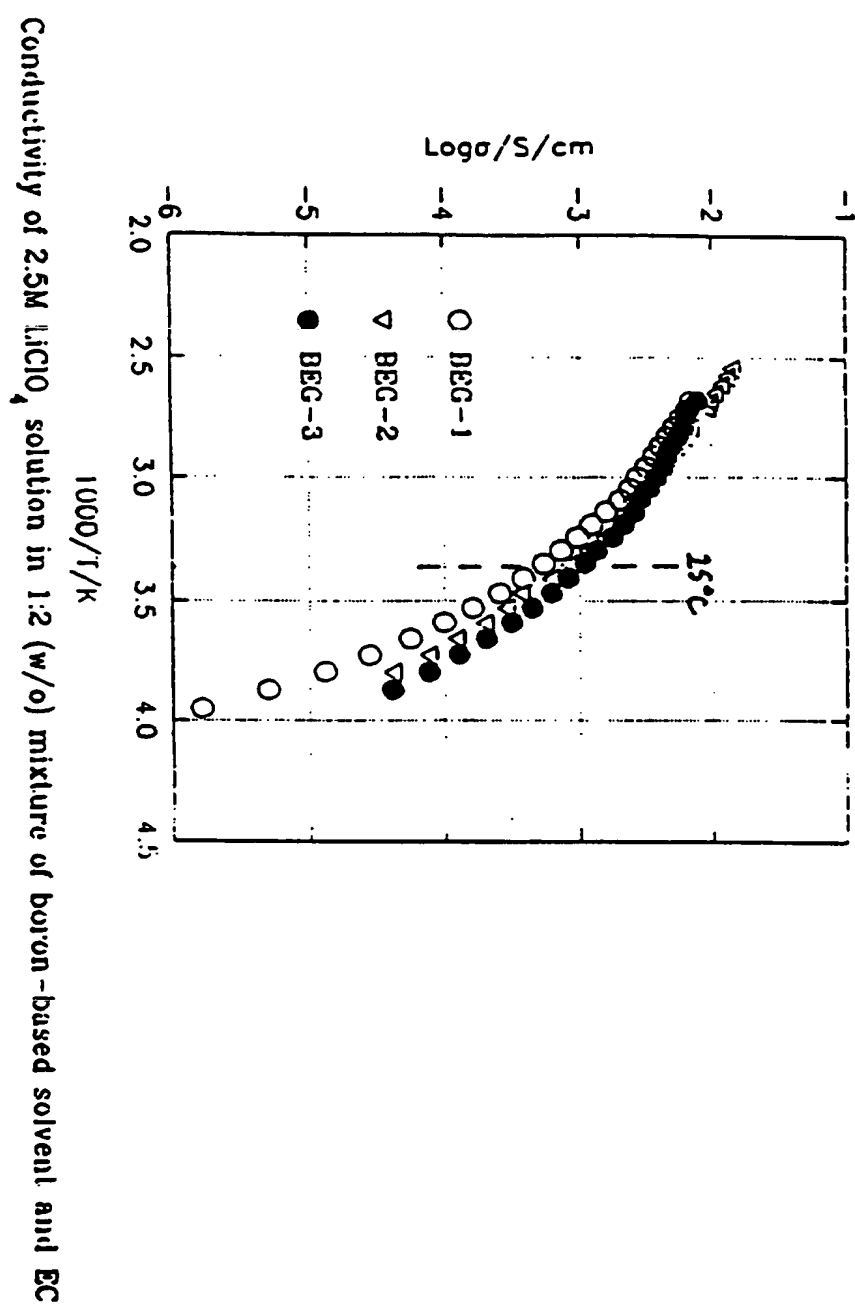
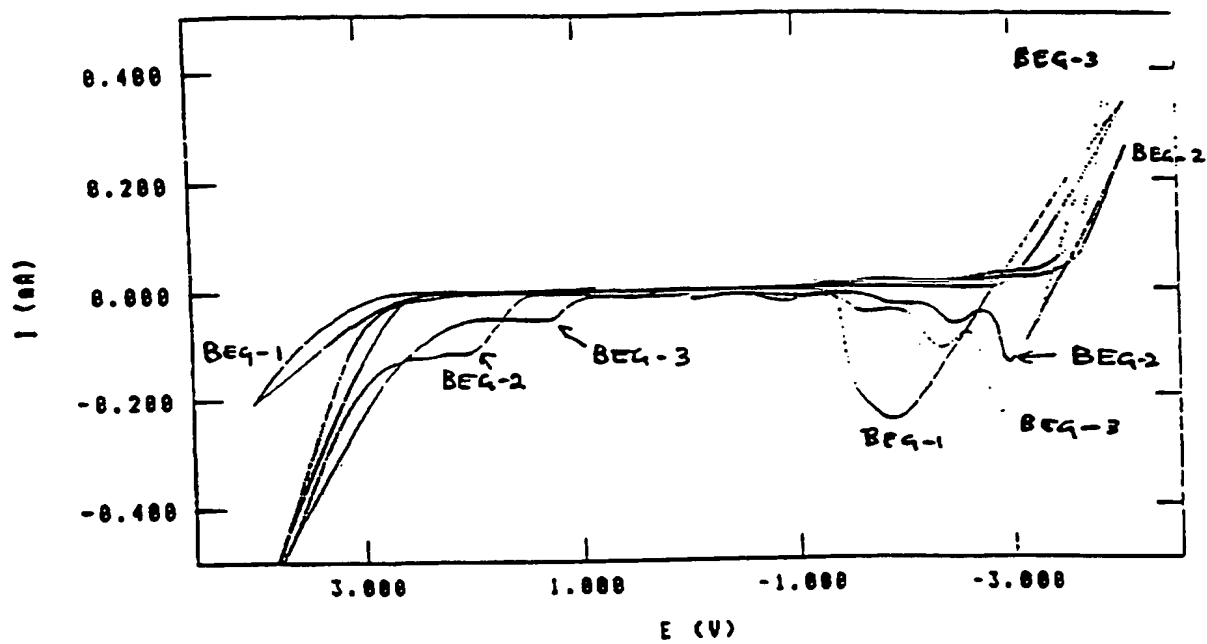
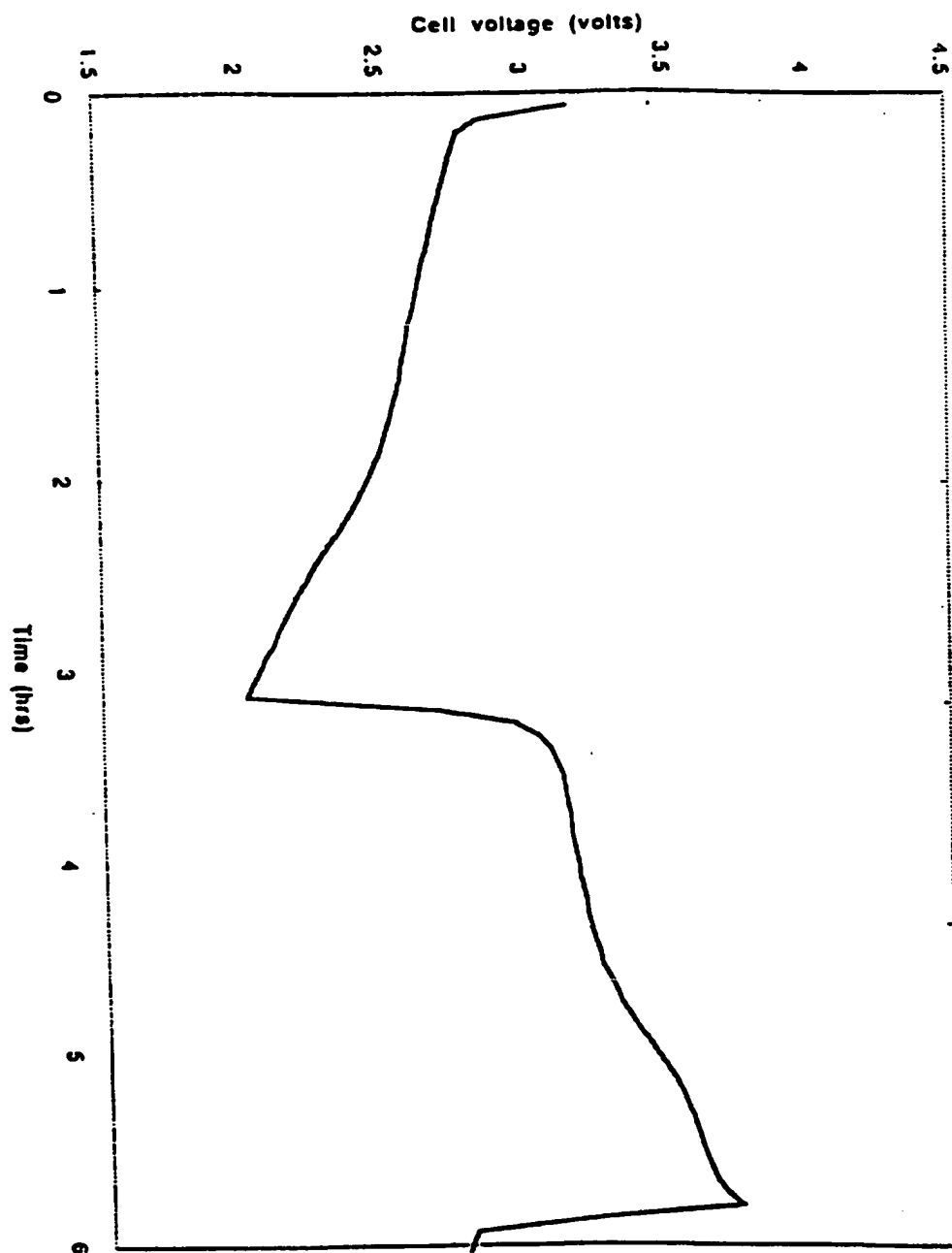


FIGURE 10

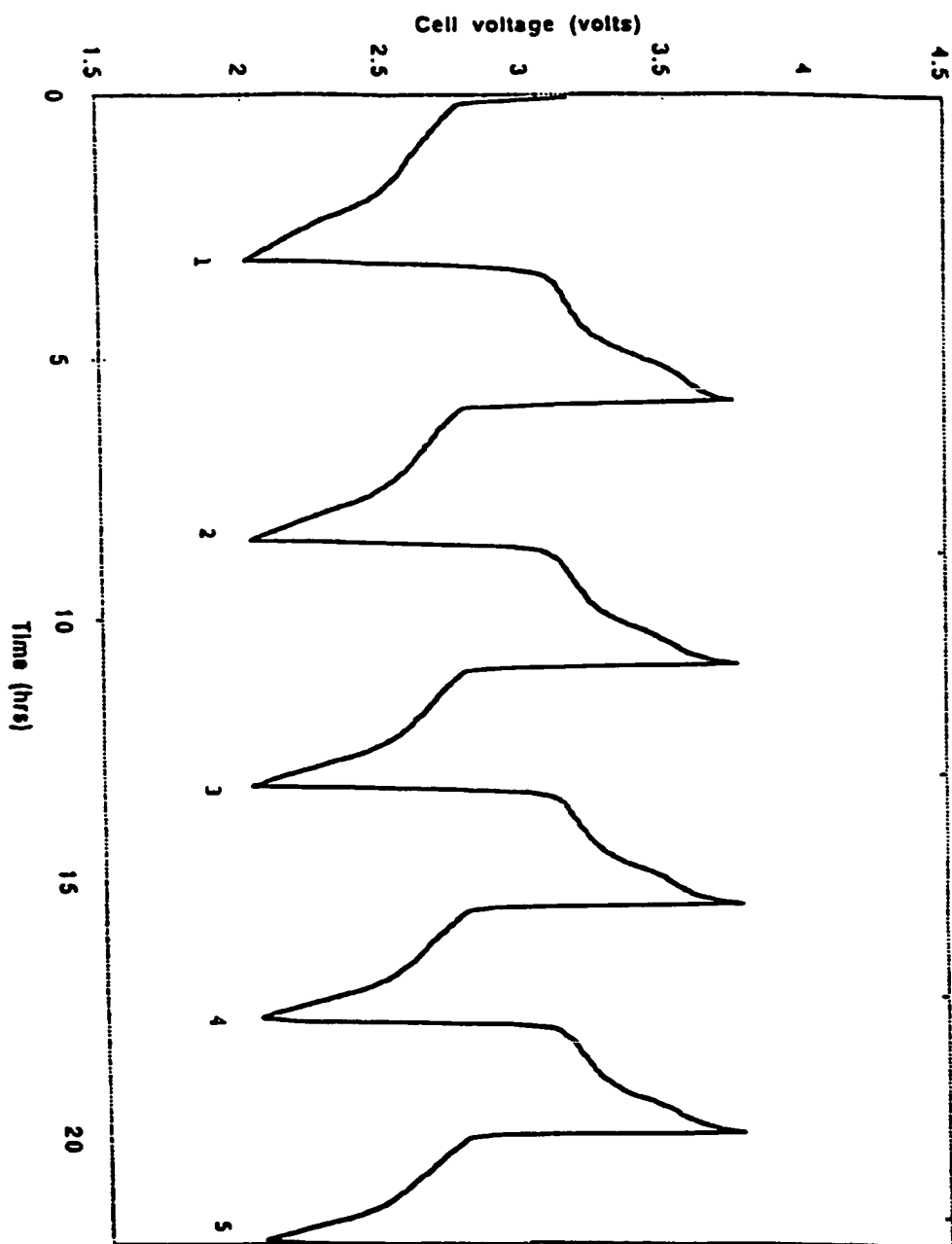


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FIGURE 11



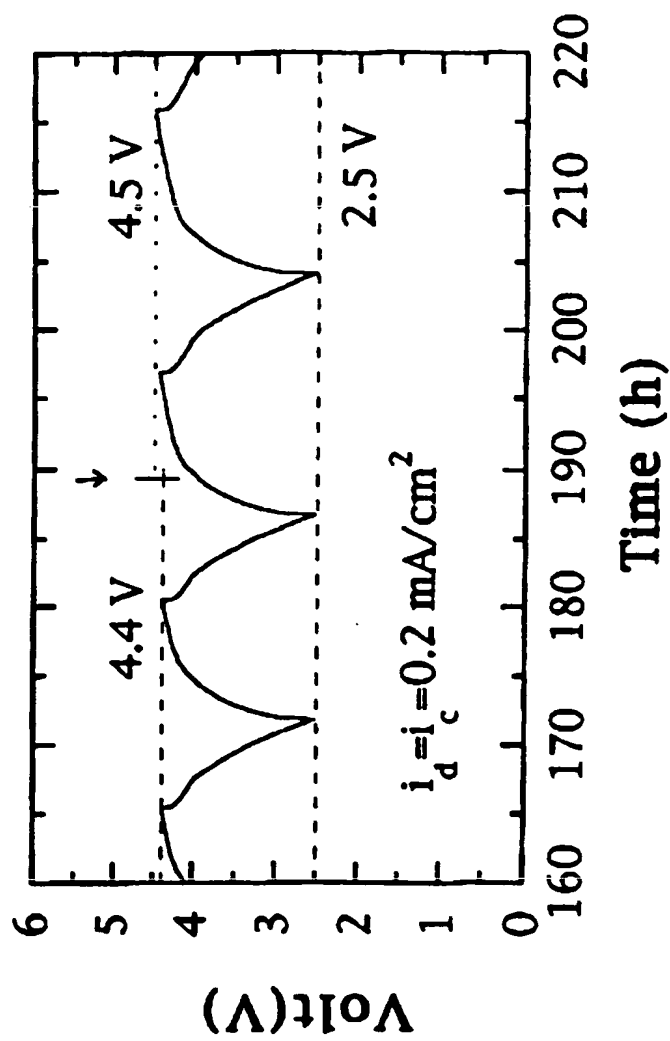
First discharge/charge curve for L1 / BEG-1 polymer gel electrolyte / LiMn2O4 battery. Area = ca. 1.0cm², run at room temperature (27°C)

12/13
FIGURE 12

Initial discharge/charge curves for Li / BSC-1 polymer gel electrolyte / Li₂Mn₂O₄ battery. Area = ca. 1.0cm², runs at room temperature (27°C)

FIGURE 13

C/Li⁺-salt in BEG-1/LiCoO₂_x



INTERNATIONAL SEARCH REPORT

International application No.
PCT/US96/17490

A. CLASSIFICATION OF SUBJECT MATTER

IPC(6) : H01M 6/14, 6/16, 6/04

US CL : 429/190, 192, 194, 198, 199

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

U.S. : 429/190, 192, 194, 198, 199

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	US 4,516,317 A (BAILEY) 14 MAY 1985, see abstract; col. 3, line 42 - col. 5, line 32.	1, 2, 10-12, 20
Y	US 4,713,151 A (SMITH) 15 DECEMBER 1987, see col. 5, line 9 - col. 6, line 40.	1, 2, 9-12, 19, 20
Y	US 4,894,302 A (HOFFMAN ET AL) 16 JANUARY 1990, see abstract.	1, 2, 9-12, 19, 20

☐ Further documents are listed in the continuation of Box C. ☐ See patent family annex.

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27 JANUARY 1997Date of mailing of the international search report
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